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(54) Title: HYDROALCOHOLIC COSMETIC MICROEMULSIONS

(57) Abstract

A hydroalcoholic microemulsion composition is provided which includes water, a C₁-C₄ alkanol and an oil material selected from vitamin oils, C₁₀-C₆₀ terpenes and mixtures thereof. The composition is formed into a clear, storage stable microemulsion through a combination of surfactants including an ethoxylated castor oil and a propoxylated alkyl ether. Especially useful is a combination of PEG-40 hydrogenated castor oil with either PPG-10 cetyl ether, PPG-10 butanediol or PPG-14 butyl ether.

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Hydroalcoholic cosmetic microemulsions.

5 The invention relates to hydroalcoholic microemulsion comprising vitamins and essential oils which exhibits excellent physical stability and clarity.

10 A clear, skin care product that contains water and alcohol conveys a sense of purity to the consumer. The presence of alcohol also imparts quick drying and cooling sensation characteristics. The use of alcohol is also important for many therapeutic products as it will solubilize certain organic acids such as salicylic acid. Antimicrobial activity is a further benefit.

15 Many therapeutic cosmetic ingredients are water-insoluble, e.g. vitamins and essential oils. These water-insoluble ingredients require them to be emulsified into a water phase in order to be effectively delivered to the skin.

20 Emulsions tend to be opaque or white because of the large droplet size. Microemulsions consist of micelles of a monolayer of surfactant surrounding an oil droplet. These micelles are small enough so that they do not appreciably diffract light producing a clear product. Alcohol is known

25 to prevent the formation of both emulsions and micelles; indeed, alcohol is commonly used to break emulsions. Formation of a microemulsion that is stable in a hydroalcoholic system is, therefore, quite difficult. Furthermore, the vitamin oils, in particular, are very

30 difficult to form microemulsions with.

The present invention provides cosmetic microemulsion composition comprising:

35 i) from 1 to 99% water;

ii) from 1 to 99% of a C₁-C₄ alkanol;

- iii) from 0.1 to 20% of an oil selected from vitamin oils, C₁₀-C₆₀ terpenes and mixtures thereof;
- iv) from 0.1 to 20% of castor oil ethoxylated with 30 to 55 of ethylene oxide per mole of castor oil; and
- v) from 0.1 to 20% of a C₄-C₂₀ mono- or dihydric alkanol propoxylated with 5 to 50 moles of propylene oxide per mole of alkanol.

Such a cosmetic microemulsion is both quick drying and imparts a cooling sensation. The micelles of the microemulsions of the invention are sufficiently small that they do not appreciably diffract light, thereby producing a clear product. The hydroalcoholic microemulsions of the invention are storage stable.

The inventors have found that hydroalcoholic cosmetic microemulsions of good clarity and stability capable of suspending vitamin oils and C₁₀-C₆₀ terpenes may be prepared using a combination of a ethoxylated, hydrogenated castor oil and at least one propoxylated alkyl ether.

Accordingly, a first critical component of compositions according to the present invention is an ethoxylated castor oil, preferably an ethoxylated hydrogenated castor oil. The moles of ethylene oxide per mole of castor oil will generally range from 30 to 55, preferably between 37 and 43, optimally 40 moles of ethylene oxide. Amounts of the ethoxylated castor oil will generally range from 0.1 to 20%, preferably from 1 to 10%, optimally from 2 to 5% by weight of the composition. Most preferred is PEG-40 hydrogentated castor oil.

A second critical component of compositions according to the present invention is that of a propoxylated alkyl

ether. Conveniently the ether is based upon a C₄-C₂₀ mono- or dihydric alkanol. Most preferred are the propoxylated butyl and cetyl alcohols and butanediols. The amount of propylene oxide per mole of alkanol will generally range from 5 to 50, preferably from 8 to 20, optimally from 8 to 12 moles propylene oxide. Amounts of the propoxylated alkyl ether will generally range from 0.1 to 20%, preferably from 1 to 10%, optimally from 2 to 5% by weight of the composition. Most preferred are the species PPG-10 cetyl ether and PPG-14 butyl ether and PPG-10 Butanediol.

The hydroalcoholic microemulsion compositions of the present invention will also include water in amounts of from 1 to 99%, preferably from 25 to 75%, optimally from 30 to 60% by weight.

Alcohols suitable for the hydroalcoholic microemulsion compositions of the present invention include the C₁-C₄ monohydric alkanols. Most preferred is ethanol. The monohydric alkanols will generally be present in amounts of from 1 to 99%, preferably from 15 to 70%, optimally from 25 to 55% by weight.

Another component of the hydroalcoholic microemulsion compositions of the present invention will be that of a skin nutritive oil material. The material will conveniently be selected from vitamin oils, C₁₀-C₆₀ terpenes and mixtures thereof. Levels of these materials may suitably range from 0.1 to 20%, optimally between 1 and 3% by weight.

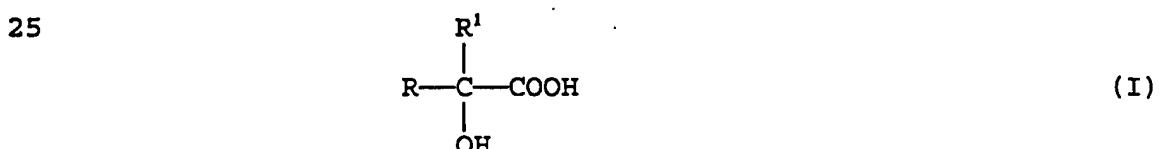
Representative of the vitamin oils are vitamin A palmitate, vitamin E linoleate, vitamin E acetate and combinations thereof. The C₁₀-C₆₀ terpene may be either a hydrocarbon or oxygenated derivative thereof. The terpene may be a monoterpane, a sesquiterpene, a diterpene or triterpene. Representative of the hydrocarbon terpenes are limonene,

pinene, myrcene, caryophyllene, farnesene, lycopene, squalene, zingiberene, carotene, camphene, cedrene and mixtures thereof. Representative of the oxygenated terpenes are geraniol, farnesol, linalool, citronellal, 5 menthol, carvone, camphor, nerol, neral, geranial, thujone, isonorborneol, isoborneol, phytol, bisabolol and mixtures thereof.

10 Hydroalcoholic microemulsion compositions of the present invention may include or be included with a variety of other cosmetic components. Suitable components are described below.

15 The first category is represented by C_7 - C_{30} β -hydroxy carboxylic acids and their salts. Illustrative of this category is salicylic acid as well as the alkali metal and ammonium salts thereof. Suitable amounts of salicylic acid or salt forms may range from 0.1 to 10%, preferably between 0.8 and 2.5%, optimally between 1 and 1.5% by weight.

20 The second category of keratolytic agent is represented by C_1 - C_{25} α -hydroxy carboxylic acids of Formula I, having the structure:



30 wherein R and R^1 are H, F, Cl, Br, alkyl, aralkyl or aryl groups of saturated or unsaturated, isomeric or nonisomeric, straight or branched chain, having 1 to 25 carbon atoms, or cyclic form having 5 or 6 ring members, and in addition, R and R^1 may carry OH, CHO, COOH and alkoxy groups having 1 to 9 carbon atoms, the α -hydroxyacid existing as a free acid or lactone form, or in salt form with an organic amine base or an inorganic alkali, and as

stereoisomers, and D, L, and DL forms when R and R¹ are not identical.

5 Most preferred of this group of materials are glycolic acid, lactic acid and 2-hydroxyoctanoic acid and salts thereof. The salts may conveniently be selected from alkali metal, ammonium and C₁-C₂₀ alkyl or alkanol ammonium counterions. Levels of α -hydroxyalkanoic acids may suitably range from 0.1 to 10%, preferably between 0.2 and 10 1%, optimally between 0.4 and 0.5% by weight.

15 In a particularly preferred embodiment, there will be present a mixture of both a β -hydroxy carboxylic acid and an α -hydroxy carboxylic acid. For instance, the optimum combination is a mixture of salicylic acid and glycolic acid in a relative weight ratio of from 20:1 to 1:20, preferably from 10:1 to 1:1, optimally from 3:1 to 2:1.

20 A still further component of compositions according to the present invention may be C₁-C₁₀ alkyl lactates. Most preferred is ethyl lactate which may suitably be present in amounts ranging from 0.01 to 5%, preferably between 0.5 and 3%, optimally between 1.5 and 2.5% by weight.

25 Antimicrobial agents may also be useful in compositions of the present invention. Typically the antimicrobial agent may be material such as triclosan tricarbanilide, tea tree oil, farnesol, farnesol acetate, hexachlorophene, C₄-C₂₀ quaternary ammonium salts such as benzolconium chloride and a variety of zinc or aluminum salts. Typically the zinc or aluminum salts are compounds such as zinc pyridinethione, zinc sulphate, zinc chloride, zinc phenolsulphonate, aluminum chloride, aluminum sulphate and aluminum chlorhydrate. Amounts of the astringent may typically range from 0.1 to 5%, preferably from 0.2 to 1%, optimally 30 0.3% by weight.

35

Emollient materials in the form of silicone oils and synthetic esters may be incorporated into compositions of the present invention. Amounts of the emollients may typically range anywhere from 0.1 to 30%, preferably 5 between 1 and 20% by weight.

Silicone oils may be divided into the volatile and non-volatile variety. The term "volatile" as used herein refers to those materials which have a measurable vapor 10 pressure at ambient temperature. Volatile silicone oils are preferably chosen from cyclic or linear polydimethylsiloxanes containing from 3 to 9, preferably from 4 to 5, silicon atoms.

15 Linear volatile silicone materials generally have viscosities less than 5 centistokes at 25°C while cyclic materials typically have viscosities of less than 10 centistokes.

20 Nonvolatile silicone oils useful as an emollient material include polyalkyl siloxanes, polyalkylaryl siloxanes and polyether siloxane copolymers. The essentially non-volatile polyalkyl siloxanes useful herein include, for example, polydimethyl siloxanes with viscosities of from 5 25 to 100,000 centistokes at 25°C. Among the preferred non-volatile emollients useful in the present compositions are the polydimethyl siloxanes having viscosities from 10 to 400 centistokes at 25°C.

30 Among the ester emollients are:

(1) Alkenyl esters of fatty acids having 10 to 20 carbon atoms. Examples thereof include oleyl myristate, oleyl stearate, and oleyl oleate.

35 (2) Ether-esters such as fatty acid esters of ethoxylated fatty alcohols.

(3) Polyhydric alcohol esters. Ethylene glycol mono and di-fatty acid esters, diethylene glycol mono- and di-fatty acid esters, polyethylene glycol (200-6000) mono- and di-fatty acid esters, propylene glycol mono- and di-fatty acid esters, polypropylene glycol 2000 monooleate, polypropylene glycol 2000 monostearate, ethoxylated propylene glycol monostearate, glyceryl mono- and di-fatty acid esters, polyglycerol poly-fatty esters, ethoxylated glyceryl monostearate, 1,3-butylene glycol monostearate, 1,3-butylene glycol distearate, polyoxyethylene polyol fatty acid ester, sorbitan fatty acid esters, and polyoxyethylene sorbitan fatty acid esters are satisfactory polyhydric alcohol esters.

(4) Wax esters such as beeswax, spermaceti, myristyl myristate, stearyl stearate.

(5) Sterols esters, of which cholesterol fatty acid esters are examples thereof.

Humectants of the polyhydric alcohol-type may also be included in the compositions of this invention. The humectant aids in increasing the effectiveness of the emollient, reduces scaling, stimulates removal of built-up scale and improves skin feel. Most especially for purposes of this invention, polyhydric alcohols enhance penetration of water-phase dissolved actives (e.g. the hydroxycarboxylic acids, alkyl lactates and antimicrobials). Typical polyhydric alcohols include glycerol, polyalkylene glycols and more preferably alkylene polyols and their derivatives, including propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol and derivatives thereof, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1,3-butylene glycol,

1,2,6-hexanetriol, ethoxylated glycerol, propoxylated glycerol and mixtures thereof. For best results the humectant is preferably propylene glycol. The amount of humectant may generally range anywhere from 0.5 to 30%, 5 preferably between 1 and 15% by weight of the composition.

Thickeners/viscosifiers, typically in amounts up to 5% by weight of the composition may also be included. As known to those skilled in the art, the precise amount of 10 thickeners can vary depending upon the consistency and thickness of the composition which is desired. Exemplary thickeners are xanthan gum, sodium carboxymethyl cellulose, hydroxyalkyl and alkyl celluloses (particularly hydroxypropyl cellulose), and cross-linked acrylic acid 15 polymers such as those sold by B.F. Goodrich under the Carbopol trademark.

Cosmetic compositions of the present invention may be 20 included in many product forms. These forms may include lotions, creams, sticks, roll-on formulations, mousses, aerosol sprays, pad-applied formulations, and overnight, peelable facial masks.

A particularly preferred embodiment of the present 25 invention is that the hydroalcoholic microemulsion compositions be incorporated into a quick-drying gel or paste that forms a peelable facial mask. A film-forming and an adhesion promoting polymer are necessary in this product form. Polyvinyl alcohol can serve as the film-forming polymer. Preferably the polyvinyl alcohol will be present as a low and high molecular weight species. The former will have a number average molecular weight ranging from 15,000 to 27,000. The higher polyvinyl alcohol 30 material will have a number average molecular weight ranging from 44,000 to 65,000. These materials are available from the Air Products Company under the trademark, Airvol 205S[®] and Airvol 523[®]. Amounts of total 35

polyvinyl alcohol will typically range from 2 to 40%, preferably from 10 to 20%, optimally between 10 and 15% by weight. The ratio of low to high molecular weight may conveniently range from 1:20 to 20:1, preferably from 1:10 to 1:1, optimally from 1:5 to 1:3, respectively.

As the adhesion promoting polymer, it is preferable to employ a hydrophobic acrylate or methacrylate polymer. Especially useful is Pemulen TR2® from the B.F. Goodrich Company. The CTFA name is acrylates/C₁₀-C₃₀ alkyl acrylate cross-polymer. The adhesion-promoting polymer will generally be present in amounts from 0.1 to 20%, preferably from 0.5 to 5%, more preferably from 1 to 2% by weight.

The following examples will more fully illustrate select embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight unless otherwise indicated.

EXAMPLE 1

5 A series of solubilization tests were conducted on hydroalcoholic microemulsion compositions to determine the best surfactant. The basic water and oil phases utilized throughout the experiments were as follows.

Water Phase

10	INGREDIENTS	WEIGHT %
	Water	37
	SD-40 Alcohol	35
	Ethyl Lactate	8
	Propylene Glycol	3
15	Lactic Acid	1
	Glycolic Acid	0.5
	Salicylic	0.5
	Zinc Sulphate	0.3
	Propylene Glycol	0.3
20	α -Hydroxycaprylic Acid	0.1

Oil Phase

	INGREDIENTS	WEIGHT %
5	Vitamin A Palmitate	0.5
	Vitamin E Linoleate	0.5
	Vitamin E Acetate	0.5
	α -Bisabolol	0.5
	Tea Tree Oil	0.3
	Eucalyptus Oil	0.1

10

The following grading system was used to determine clarity and stability:

15 0 = No emulsion (2 phases)
 1 = White emulsion, breaks after 24 hours
 2 = Opaque emulsion, stable
 3 = Clear microemulsion, clouds after 24 hours
 4 = Clear microemulsion, stable at 50°C or 2 months

20

TABLE I

SURFACTANT (all at 4%)		GRADE
5	PEG-2 Oleyl Ether	0
	PEG-20 Oleyl Ether	1
	PEG-10 Oleyl Ether	1
	PEG-10 Oleyl Ether Phosphate	0
	PEG-20 Isocetyl Ether	0
	PEG-40 Stearate	0
10	PEG-20 Dilaurate	0
	PEG-20 Glycereth	1
	PEG-7 Glycereth	1
	PEG-45 Palm Kernel Glycerides	1
	PEG-60 Almond Glycerides	0
15	PEG-60 Sorbitan Tetraoleate	0
	PEG-21 Stearate	0
	Nonoxynol-9	1
20	Nonoxynol-10	1
	Nonoxynol-12	1
	Nonoxynol-15	1
	Octoxynol-9	2
25	Polaxamer-338	3
	Polaxamer-407	1
	Polaxamer-185	1
	Polaxamer-182	1
	Polaxamer-331	2
30	Polaxamer-188	2
	Polaxamer-108	1
	Polaxamer-131	1
	Polaxamer-401	0
	Polaxamer-335	0
35	Nitrol Pen-4612	2
	Nitrol Pen-4630	3
40	Polysorbate-20	0
	Polysorbate-60	0
	Polysorbate-80	0
	Polysorbate-81	0
	Polysorbate-85	1

Table I (continued)

SURFACTANT (all at 4%)		GRADE
5	Isocetyl PPG-2 PEG-20 Acetate	1
	Procetyl-AWS	2
	PPG-10 Cetyl Ether	3
10	PPG-50 Cetyl Ether	1
	PEG-7 Hydrogenated Castor Oil	1
	PEG-35 Hydrogenated Castor Oil	2
15	PEG-40 Hydrogenated Castor Oil	3
	PEG-43 Hydrogenated Castor Oil	2
	PEG-54 Hydrogenated Castor Oil	2
	PEG-60 Hydrogenated Castor Oil	1

TABLE II

COMBINATION SYSTEMS (all at 3% and 3%)		GRADE
5	PEG-40 Hydrogenated Castor Oil (3%) with...	
	PPG-10 Cetyl Ether (1.5%)	4
	PPG-10 Cetyl Ether	3
	PPG-50 Cetyl Ether	2
	PPG-10 Cetyl Ether Phosphate	2
10	PEG-6000 Monostearate	1
	Glycereth-7	1
	Glycereth-26	2
15	Octoxynol-9	2
	Nonoxynol-100	3
20	PPG-5 Ceteth-20	2
	Abil Wax 8851	2
	Abil Wax 8852	3
	Abil Wax 8873	2
25	Pecosil PS100	1
	Pecosil PS100ad	1
	Pecosil PS100K	2
30	Polysorbate-80	2
	PPG-10 Butanediol	4
	PPG-12 Buteth-16	2
	PPG-28 Buteth-35	2
35	PPG-9 Buteth-10	3
	PPG-14 Butyl Ether	3
	Poloxamer-181	1
	Poloxamer-401	2
40	Poloxamer-338	2

TABLE II (continued)

COMBINATION SYSTEMS (all at 3% and 3%)		GRADE
5	PPG-10 Cetyl Ether with...	
	PEG-6000 Monostearate	1
10	Glycereth-26	2
	Glycereth-7	3
15	Poloxamer-338	3
	Nikkol Pen-4630	3
20	PPG-10 Butyl Ether	2
	PEG-45 Hydrogenated Castor Oil	2
	PEG-54 Hydrogenated Castor Oil	2
	PEG-7 Hydrogenated Castor Oil	2

Based upon the experiments in the above Tables, it is evident that the best combinations are PEG-40 hydrogenated castor oil with either PPG-10 cetyl ether, PPG-10 butanediol or PPG-14 butyl ether.

The foregoing description and examples illustrate selected embodiments of the present invention. In light thereof, various modifications will be suggested to one skilled in the art, all of which are within the spirit and purview of this invention.

CLAIMS

1. A Cosmetic microemulsion composition comprising:

- 5 i) from 1 to 99% water;
- ii) from 1 to 99% of a C₁-C₄ alkanol;
- 10 iii) from 0.1 to 20% of an oil selected from vitamin oils, C₁₀-C₆₀ terpenes and mixtures thereof;
- iv) from 0.1 to 20% of castor oil ethoxylated with 30 to 55 moles of ethylene oxide per mole of castor oil; and
- 15 v) from 0.1 to 20% of a propoxylated alkyl ether comprising a C₄-C₂₀ mono- or di-hydric alkanol propoxylated with 5 to 50 moles of propylene oxide per molecule of alkanol.

20 2. A composition according to claim 1 wherein the vitamin oils comprises vitamin A palmitate, vitamin E linoleate, vitamin E acetate and mixtures thereof.

25 3. A composition according to claim 1 or claim 2 wherein the terpene comprises a hydrocarbon selected from limonene, pinene, myrcene, caryophyllene, farnesene, lycopene, squalene, zingiberene, carotene, camphene, cedrene and mixtures thereof.

30 4. A composition according to claim 1 or claim 2 wherein the terpene comprises an oxygenated terpene selected from geraniol, farnesol, linalool, citronellal, menthol, carvone, camphor, nerol, neral, geranial, thujone, 35 isonorborneol, isoborneol, phytol, bisabolol and mixtures thereof.

5. A composition according to any one of claims 1 to 4 wherein water is present in an amount of from 30 to 60% by weight.
- 5 6. A composition according to any one of claims 1 to 5 wherein the monohydric alcohol is ethanol present in an amount of from 25 to 55% by weight.
- 10 7. A composition according to any one of claims 1 to 6 wherein the oil is present in an amount of from 1 to 3% by weight.
- 15 8. A composition according to any one of claims 1 to 7 wherein the ethoxylated castor oil is PEG-40 hydrogenated castor oil.
9. A composition according to any one of claims 1 to 8 wherein the propoxylated alkyl ether comprises PPG-10 cetyl ether, PPG-10 butanediol and PPG-14 butyl ether.
- 20 10. A composition according to claim 9 wherein the ethoxylated castor oil and the propoxylated alkyl ether are each present in an amount of from 1 to 5% by weight.

INTERNATIONAL SEARCH REPORT

Int. Application No
PCT/EP 94/02519A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/00 A61K7/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	<p>EP,A,0 571 677 (UNILEVER PLC) 1 December 1993</p> <p>see page 2, line 42 - line 47</p> <p>see page 4, line 29 - line 42</p> <p>see page 5, line 12 - line 16</p> <p>see page 5, line 21 - line 31</p> <p>see page 6, line 2 - line 21</p> <p>see claims 1--1 13-21; examples 1,2</p> <p>---</p> <p>-/-</p>	1,3-5,7, 8

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/EP 94/02519

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 92, no. 10, 10 March 1980, Columbus, Ohio, US; abstract no. 82190, M. TAGAWA 'The effect of ethanol on the solubilization of limonene by nonionic surfactants' see abstract & J. SOC. COSMET. CHEM. JAPAN, vol.13, no.1, 1979 pages 47 - 51 M. TAGAWA</p> <p>---</p>	1-10
A	<p>EP,A,0 261 351 (ROURE BERTRAND DUPONT SOCIÉTÉ ANONYME) 30 March 1988 see the whole document</p> <p>-----</p>	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/EP 94/02519

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